EXHIBIT A

PULP AND PAPER

Chemistry and Chemical Technology

SECOND EDITION
Revised and Enlarged

JAMES P. CASEY

Director of Starch Sales, Union Starch and Refining Company, Columbus, Indiana. Formerly Director of Applications Research, A. E. Staley Manufacturing Company, Decatur, Illinois. Formerly Associate Professor, Pulp and Paper Department, State University of New York, College of Forestry, Syracuse, New York

VOLUME II:
Papermaking

INTERSCIENCE PUBLISHERS, INC., NEW YORK

a division of John Wiley & Sons, Inc., New York · London · Sydney

SURFACE SIZING

In the last chapter, internal sizing was discussed. In this chapter, a different form of sizing, known as surface sizing, is described. Surface sizing is an ancient operation as old as papermaking itself. In fact, the word "sizing" is often defined by lexicographers in the sense of applying glue to paper surfaces.

Effect of Surface Sizing on the Properties of Paper

Surface sizing differs from internal sizing in that the sizing agent, e.g., animal glue or starch, is applied to the surface of the paper where it cements the fibers to the body of the paper and deposits a more or less continuous film on the paper surface. The advantage of surface sizing is that a smooth hard film is produced on the surface of the paper which will not catch the pen when the paper is written upon and will not pick if the paper is printed with tacky inks. Furthermore, the oil resistance of the paper is increased, since the surface pores of the paper are sealed. Surface sizing is oftentimes more important than internal sizing for writing papers, printing papers, and certain grades of wrapping papers.

Types of Surface-Sizing Agents Used

The two principal surface-sizing agents used commercially are starch and animal glue, starch being used to the greatest extent. Other sizing agents include methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, wax emulsions, and a variety of new resin polymers which are sometimes used to obtain special effects. Surface-sizing agents can be applied in a size press, in a size tub, or (in the case of heavy papers) at the calenders. The various methods of applying surface-sizing agents will be discussed later in this chapter.

Surface sizing is primarily concerned with surface films, and consequently it is usually desirable to keep the size on the surface of the paper as much as possible, where it will do the most good. This is particularly true when using expensive sizing agents such as poly-

vinyl alcohol, carboxymethyl cellulose, and even animal glue. On the other hand, it is desirable on some grades of paper, when starch is the sizing agent, to obtain considerable penetration of starch into the paper in order to build up the burst, internal sizing, and other internal properties of the sheet. Commercial papers surface-sized with starch vary from papers showing very little penetration to papers where the starch has penetrated completely through the sheet.[1,2]

Surface-sized papers should not be visualized as having a continuous film covering the entire surface, because this condition is rarely attained. Lee[1,2] has noted that starch covers the surface fibers very irregularly, being thin in some spots and dense in others, so that a continuous film is not obtained unless a high concentration of starch is applied. Most commercial papers surface-sized with starch have a somewhat uneven, discontinuous film of starch on their surface. Animal glue appears to form a better film than starch, but as a rule it, too, does not form a completely unbroken film, although in rare cases a uniform, fairly continuous film may be obtained.[1] On the other hand, some of the better film-forming substances, such as polyvinyl alcohol, zein, methyl cellulose, and carboxymethyl cellulose tend to produce a sizing layer which more nearly approaches a continuous film. The film of sizing agent is, however, often broken by the presence of fibers protruding from the surface of the sheet.

Effect of Surface Sizing on Water Resistance

Surface sizing with starch does not materially increase the water resistance of the paper, and even with animal glue there is only a slight increase in the water resistance. The low water resistance of these materials is due to their low angle of contact with water. However, water resistance is not particularly desired in surface sizing, since the primary purpose of the size is to make the paper resistant to colloidal solutions (writing inks) or to oily vehicles (printing inks). It should be pointed out that two papers with the same internal sizing (as measured by the water penetration test) may differ greatly in surface sizing (as measured by writing qualities of the paper).

Papers to be printed by the offset process are usually surface-sized with starch in order to prevent the loosening of surface fibers during moistening of the paper with water on the press. According to

Cobb,[3] surface films of starch increase the sensitivity of offset papers to changes in the relative humidity of the atmosphere, but starch-sized papers are useful for offset printing because it is possible, by sizing with starch, to use stock which has been beaten to a lesser degree. In this way, advantage is taken of the functional properties of the starch film which produces a hard, slightly water-resistant surface over a softer, freer body stock. Surface sizing was found by PATRA (Printing, Packaging, and Allied Trades Research Association) to be the most effective means of reducing fluffing in offset papers.[3a] Increasing the ratio of softwood to hardwood fiber and increased beating also reduce fluffing, but these tend to lower dimensional stability and reduce opacity.

A number of other special grades of paper are surface-sized commercially for special or unusual effects. One special case which might be mentioned is the surface treatment of paper with starch or glue to produce alkali-proof papers for use as soap wrappers. In this application, the sizing prevents the alkali in the soap from discoloring the paper or destroying the rosin in the sheet.[4] The degree of protection required depends upon the amount of free alkali and the moisture content of the soap. Low iron content in the paper is important in preventing discoloration.

Although the conventional surface sizing agents, such as starch and animal glue, do not impart water resistance, there are a number of newer sizing agents which do. Some of these will actually impart water repellency. They are not widely used, and find application only when special effects are required. Their use is discussed later in this chapter. It should be pointed out that there are special cases where surface water absorption characteristics may be more important than internal sizing. Stephenson[4a] mentions flexographic printing as one case, since many flexographic inks are water emulsions.

Effect of Surface Sizing on Penetration of Oils

The penetration of oils into paper is important in papers to be printed with high gloss inks, papers to be coated with paraffin, or papers to be used in contact with greasy foods. The most oil-resistant papers are those papers of very low porosity (glassine and greaseproof papers), or those papers which have been surface sized with a film of oil-resistant material. Surface sizing with starch, animal glue, carboxymethyl cellulose, polyvinyl alcohol, or similar materials is used commercially for producing papers which must be resistant to oily materials. These sizing agents are effective because they increase the contact angle against oil and provide a relatively continuous and nonporous film through which the oil cannot penetrate.

The oil resistance of paper is generally measured by the time required for an oily test liquid to penetrate through the paper. For best results, the paper should be tested against the material with which it comes into contact during use, but in many cases turpentine is used to speed up the test.

The standard turpentine test is based upon the time required for water-free turpentine to penetrate through the test specimen and discolor an underlying sheet of book paper. In carrying out this test, 1.1 ml. of turpentine (which has been colored red with an oil-soluble dye) is added to a pile of sand (5 g.) on top of the test specimen, and the time is taken for complete penetration through the paper. The turpentine test shows up pinholes or other mechanical defects on the surface of the paper.

The results of the turpentine test do not correlate well with the resistance of the paper to oily materials of high viscosity, e.g., printing inks. This is shown in Figure XIV-1,[5] where the resistance to the penetration of oils of varying viscosity is shown for papers surface-sized with different amounts of carboxymethyl cellulose. It can be seen from these results that it is possible to have a considerable difference in oil resistance between samples when tested with high viscosity oils, but little difference when tested with low viscosity oils. The amount of moisture present in the test liquid affects the rate of oil penetration, although the initial penetration may not be greatly changed.[6]

In another test for oil resistance, a glass or metal ring is sealed to the test specimen with corn syrup, the assembly placed on a piece of white paper on a glass plate, and the ring filled to a height of 1 in. with oil which has been dyed red. Periodic examination is made to determine when the oil has penetrated the test specimen and stained the white paper. An accelerated test may be carried out in a warm air oven. Peanut oil is frequently used as the test material because of its penetrating properties. Castor oil and mineral oils are also used.

The degree of oil resistance required in commercial papers depends upon the end use of the paper. Greaseproof wrapping papers require a high degree of oil resistance and hence must be surface-sized so that there is a rather heavy, continuous film of sizing agent on the surface of the paper. These papers are often folded and creased during use, and consequently it is desirable to make the tests on creased samples to determine the flexibility of the film. Solid fats (e.g., dyed lard) may be used for testing, either by determining the time required for the complete penetration of the melted fat through the paper (thin paper), by determining the weight of the melted fat absorbed by the paper (heavy paper), or by measuring the amount of surface staining by the solid fat.

When surface sizing is used for improving the printing properties, as in the sizing of paperboard for gloss ink printing, there are definite limitations to the amount of sizing agent to be applied, since the surface absorbency of the paper must fall within definite limits, depending upon the type of ink used and the results desired in the printed paper. If too little surface size is used, the paper will absorb too much ink during printing, thereby producing a flat, unattractive printing job. On the other hand, if there is too much surface size, the ink will be slow in drying, resulting in "offset" and shiny spots. The Vanceometer is a frequently used test for measuring the degree of oil or ink resistance for gloss ink printing (see Chapter XX).

Effect of Surface Sizing on Writing Qualities

The writing qualities of paper with ink are of great importance on such grades as bond, ledger, tablet, envelope, papeterie, index bristol, chart paper, and business forms since these grades are generally written upon with pen and ink. Another grade requiring the same general qualities is paper for commercial ruling. This paper is purchased by manufacturers of blank books or stationers and is ruled with a disk ruler (for tablets and exercise books) or with a pen ruler (for ledgers or similar books requiring multicolored or discontinuous lines).

The better grades of the above papers are surface-sized, generally with starch or animal glue. Surface sizing improves the writing qualities because of the effect in increasing the contact angle,[7,8] increasing the smoothness, and reducing the porosity of the paper. The sizing agent acts as a film which "filters out" the dyestuffs in ordinary writing ink, thereby preventing "feathering" or spreading of the ink particles over the surface of the paper.

The writing qualities of paper are determined to a large extent by the type of ink used. The earliest inks were made from the juice of colored berries, and later from simple suspensions of carbon black in water with some gum or gelatin added to prevent feathering of the ink on the paper. The iron tannate inks were developed in the twelfth century and were first made from ferrous sulfate, tannin from nutgalls, and some glue or vegetable gum. These inks contain soluble ferrous–tannin compounds which are converted into insoluble ferric compounds upon exposure of the ink line to air. The dye-base inks were developed later to produce an ink which would keep indefinitely in the bottle and not form thick deposits. These inks are less permanent than other types, and for this reason, iron salts or colored metal oxides are sometimes added to provide coloring matter which exists after the organic dyestuff has faded. Record inks are a special type which are made slow-drying by the addition of glycerine. Direct dyestuffs are used in these inks because they feather less than acid or basic dyestuffs. With the development of the fountain pen, it became necessary to eliminate gum arabic and other gums from the ink, and even, in some cases, to add surface-active and hygroscopic agents in order to keep the ink free-flowing in the pen.[9] Modern, quick-drying inks, which dry within a few seconds after application to the paper, dry either through evaporation of the solvent or through penetration of the vehicle into the paper. Most of these inks contain a small amount of a nonvolatile, water-miscible, surface-active agent to promote penetration of the ink into the paper. These agents have the disadvantage that they increase the horizontal penetration, as well as the vertical penetration, thus causing feathering.[10] The ink used in ball point pens is a nonaqueous ink and can be used for writing on unsized papers. These inks do not present the sizing problems of aqueous inks, but some of them make erasing difficult without damage to the paper surface.[11] Smearing of the ink is also a problem on some papers.

The writing qualities of paper are generally measured by a simple test, termed the "pen and ink" test, which is carried out by drawing several lines on the paper in one direction and several in the op-

posite direction, using an ordinary draftsman's pen or a special pen (silver alloy pen No. 225). It is best to test the paper against the particular type or types of ink with which it is to be used, although often a standard writing ink or, in some cases, a 0.08% solution of Malachite green is used. Lack of good writing quality is manifested in these tests by feathering or spreading of the ink beyond the points of contact of the pen. A series of standardized solutions of graded wetting power may be used, and the results reported in terms of which solution first causes feathering. The sizing should be tested on both sides of the sheet, since in many cases the writing qualities may be satisfactory on the felt side and unsatisfactory on the wire side.

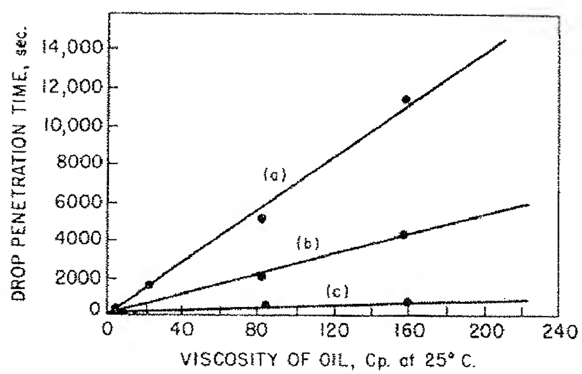

Fig. XIV-1. Effect of viscosity of oil on the oil resistance of papers surface-sized with carboxymethyl cellulose: (a) 2% solution applied at size press and 4% applied at calenders; (b) 4% solution applied at calenders; (c) no surface treatment.

The most common paper complaints in pen ruling result from defects in the paper surface.[12] A common defect, which contributes to skipping and broken lines by causing the pens to fill with fuzz and lint, is loosely bound surface fibers, but this difficulty can be eliminated by satisfactory surface sizing of the paper. Another difficulty is rough surface, arising from felt marks, wire marks, watermarks, or press roll marks. Greasy spots on the surface of the paper resulting from too much grease in animal glue surface size cause trouble with skipping, as does also the presence of slime spots. A high filler content in the paper causes excessive wear on the ruling pens, especially when abrasive fillers are used. The moisture content of the paper at the time of ruling is an important factor; a change in the relative humidity of the atmosphere in which the paper is stored from 20 to 85% may double the amount of ink spread or feathering[13] or, in other words, change the paper from fair into very poor. The dimensions of the fibers and the amount of machine to cross direction alignment affect the ruling qualities. Best results are obtained in commercial ruling, which is usually carried out in one direction only, when the lines run parallel to the fibers. In general, the ruling and writing qualities of rag papers are superior to those of sulfite or groundwood papers[14] (see "Angle of Contact Test," Chapter XIII).

Effect of Surface Sizing on Erasability

Erasability may be defined as that property of paper which permits writing to be removed from the paper by erasure without excessive erosion of the paper. Paper of good erasability should also maintain a satisfactory appearance when the erased area is written upon again. Thus, the erasability is really a composite of the resistance of the paper to the penetration of ink, resistance of the paper to abrasion, ability of the paper to maintain a smooth surface, and ability of the paper to retain sizing value after erasure.

The erasing qualities of paper are important for such grades as ledgers, bonds, stationery, drawing, and tablet, because such papers must permit writing over erased areas. These papers require a high degree of internal sizing and, also, for the best grades, a surface sizing with animal glue or starch.

The ease of erasure can be determined only after the paper has been written or printed upon with the appropriate ink, inasmuch as the erasing qualities are, to a considerable extent, related to the writing and printing qualities of the paper. There may be quite a difference between the erasing qualities of a given paper when printed or typed upon with an oil-base ink compared with those of the paper when written upon with a water-base ink. The ease of erasure may be measured by such simple methods as scraping the written area with a knife or rubbing the paper with erasing rubbers of different hardness. More elaborate tests involve the use of mechanical abrading machines such as the Taber abrader (see Chapter